



# Enhanced secondary organic aerosol formation from the photo-oxidation of mixed anthropogenic volatile organic compounds

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15 **Abstract.** Motor vehicle exhaust is one of the important contribution sources of secondary organic aerosol (SOA) in urban areas. Long-chain alkanes and aromatic hydrocarbons are included in gaseous organic pollutants of vehicle emissions, representative for diesel and gasoline vehicles respectively. In this work, the SOA production from individual anthropogenic volatile organic compounds (AVOCs) (n-dodecane, 1,3,5-trimethylbenzene) and mixed AVOCs (n-dodecane + 1,3,5-trimethylbenzene) were studied with a large-scale outdoor smog chamber. Results showed that the SOA formation from the

20 mixed AVOCs was enhanced compared to the predicted SOA mass concentration based on the SOA yield of individual AVOCs. According to the results of mass spectrometry analysis with electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS), interaction occurred between intermediate products from the two precursors, which could be the main reason for the enhanced SOA production from the mixed AVOCs reaction system. This study indicates that further studies on SOA chemistry from the mixed VOCs reaction system are needed, as the interactions between them and the effect

25 on SOA formation can give us a further understanding of the SOA formed in the atmosphere.

## 1 Introduction

Formation of secondary organic aerosol (SOA) has received considerable attention during the past few decades, as it plays an important role in affecting global climate change (Shrivastava et al., 2017; von Schneidmesser et al., 2015; Mellouki et al., 2015; Kanakidou et al., 2005), atmospheric visibility (Zhang et al., 2015a; Moise et al., 2015; Laskin et al., 2015; Ren et al., 2018), and public health (Poschl, 2005; Poschl and Shiraiwa, 2015; Zhang et al., 2016; Requia et al., 2018). The

30 formation, growth, and transformation of SOA influence the atmospheric aerosol's physicochemical properties (Poschl and Shiraiwa, 2015; Moise et al., 2015; Mellouki et al., 2015; Herrmann et al., 2015). The precursors of SOA mainly include anthropogenic volatile organic compounds (AVOCs) and biogenic volatile organic compounds (BVOCs) (Kelly et al., 2018);



in urban areas, AVOCs are the main sources of SOA, e.g., gasoline vehicle emissions (Johnson et al., 2004; Charron et al.,  
35 2019; Yang et al., 2018), diesel vehicle emissions (Paulsen et al., 2005; Wirtz and Martin-Reviejo, 2003; Odum et al., 1996;  
Zhao et al., 2015), and solvent use (Li et al., 2017c; Kansal, 2009).

Early regional air quality models underestimated the observed SOA concentrations in large areas of the atmosphere  
(Volkamer et al., 2006; Heald et al., 2005; de Gouw et al., 2005; Appel et al., 2017; Huang et al., 2017a); after incorporating  
the newly discovered SOA sources, the gap between the observed and predicted SOA concentrations is decreasing (Zhao et  
40 al., 2016; Slowik et al., 2010; Hodzic et al., 2010). The SOA formation processes in the atmosphere are very complicated;  
although the degradation of most VOCs is clear now, the formation and aging of a large amount of SOA is still unclear.  
Previous studies found that the observed organic aerosol concentration could not be explained by the traditional yields of the  
measured AVOCs (de Gouw et al., 2005); in addition, field observations found that the potential interactions between  
AVOCs and BVOCs existed during SOA formation (Spracklen et al., 2011; Hoyle et al., 2011; Glasius et al., 2011;  
45 Galloway et al., 2011; Kari et al., 2019): AVOCs could enhance (Spracklen et al., 2011; Carlton et al., 2010; Shilling et al.,  
2013) or suppress SOA formation from BVOCs (Kari et al., 2019). A recent study also found that the SOA formation could  
be reduced by the mixture of BVOCs (McFiggans et al., 2019). These findings indicate that there are interactions in the  
complex mixtures of VOCs, which may influence the SOA production estimation if they were considered in models.

In urban areas, motor vehicle exhaust is one of the important sources of SOA, the representative substances of which  
50 include aromatic hydrocarbons and long-chain alkanes (Paulsen et al., 2005; Wirtz and Martin-Reviejo, 2003; Charron et al.,  
2019; Saathoff et al., 2009; Zhao et al., 2015; Gentner et al., 2012). As an important contributor to SOA in urban areas,  
aromatic hydrocarbons are generally concerned about their kinetics (Atkinson and Arey, 2003; Calvert et al., 2002), reaction  
mechanisms (Tsiligiannis et al., 2019; J. Midey\* et al., 2003; Huang et al., 2017c; Wang et al., 2020; Garmash et al., 2019),  
SOA yield (Cao and Jang, 2007; Kroll et al., 2007; Ng et al., 2007b; Huang et al., 2017b), ozone generation potential (Luo et  
55 al., 2019), and SOA physicochemical properties (optical properties, morphology, etc.) (Grosjean, 1981; Li et al., 2018; Li et  
al., 2017b; Phillips and Smith, 2014; Kim and Paulson, 2013; Huang et al., 2018). Long-chain alkanes, as representative  
substances of intermediate volatile organic compounds (IVOCs), are considered as potential contributor of SOA (Robinson  
et al., 2007; Trostl et al., 2016; Shiraiwa et al., 2013). The studies about long-chain alkanes includes SOA chemical  
compositions (Fahnestock et al., 2015; Yee et al., 2013; Aimanant and Ziemann, 2013; Yee et al., 2012), SOA yield (Loza et  
60 al., 2014; Tkacik et al., 2012), and SOA optical properties (Li et al., 2017a; Li et al., 2020), etc. The aromatic hydrocarbons  
and long-chain alkanes are generally studied separately in the laboratory. However, it should be noted that in the real  
atmosphere, aromatic hydrocarbons and long-chain alkanes often exist at the same time, especially from vehicle emissions  
(Wu and Xie, 2018). The studies cover these two types of substances in one reaction system are still limited, and the  
corresponding SOA formation and reaction processes are not yet clear.

65 The aim of this work is to investigate the SOA formation from the mixed AVOCs reaction system. In this study, the  
SOA yield derived from n-dodecane and 1,3,5-trimethylbenzene in the presence of HONO were obtained with an outdoor  
smog chamber, and the SOA derived from the mixed AVOCs were measured. The measured SOA mass concentration from



70 mixed AVOCs reaction system was compared to the predicted SOA mass based on the SOA yield of n-dodecane and 1,3,5-trimethylbenzene. SOA particles were collected and analyzed with an electrospray ionization time-of-flight mass spectrometer (ESI-TOF-MS) to achieve insight into the chemical composition and interactions. The results here are helpful to improve our understanding of the contribution of representative precursors in the exhaust of motor vehicles to SOA.

## 2 Experimental Section

### 2.1 Experimental Methods

75 The experiments were conducted in a 56 m<sup>3</sup> (3.2 m × 6.2 m × 2.5 m) outdoor smog chamber constructed at Chinese Research Academy of Environmental Sciences (the CRAES Chamber, 40°02'27.73"N, 116°24'41.56"E). The details of the chamber had been described previously (Li et al., 2021). Briefly, the chamber was made of FEP Teflon film, the light transmission of which was above 90% at the wavelength of 350-900 nm. The substances inside the chamber could be mixed well within 4 min. The experimental duration under solar irradiation was about 7~8 h. After each experiment, the chamber was cleaned with zero air for at least 24 h with a flow rate of 200 L/min.

80 1,3,5-trimethylbenzene or n-dodecane was introduced into the chamber by zero air through the custom-made U-shaped glass tube with a known volume of liquid 1,3,5-trimethylbenzene or n-dodecane. Concentrations of 1,3,5-trimethylbenzene and n-dodecane were measured before and after reactions by collecting samples on Tenax TA solid adsorbent and analyzing by thermal desorption-gas chromatography with flame ionization detection (TD, UNITY-xr; GC, 7890B). OH precursor of the experiments was HONO, it was prepared by dropwise addition of 1 mL 2 wt% NaNO<sub>2</sub> solution into 2 mL 15 wt% 85 sulfuric acid solution in a custom-made glass bubbler, the bubbler was attached to the smog chamber with Teflon tube, and the formed HONO was introduced into the chamber by zero air. The NO, NO<sub>2</sub>, and formed ozone in the chamber were measured by NO<sub>x</sub> analyzer (EC 9841, ECOTECH, Australia) and ozone analyzer (EC 9830, ECOTECH, Australia), respectively. After the gas species mixed evenly in the chamber, the enclosure of the chamber was opened.

90 After each photochemical experiment, the formed aerosol particles in the chamber were collected by a low flow sampler (LV 40BW, Sibata Scientific Technology Ltd., Soka, Japan) at a flow rate of 5 L/min for 10 min. The PTFE filters (0.2 μm, 47 mm, MerckMillipore, TYPE FGLP) used were extracted in 5 mL methanol sonicating for 30 min. The methanol solutions were analyzed by an ESI-TOF-MS (Bruker, Impact II) in positive mode, and the chemical compositions of the formed SOA were obtained. The methanol solutions were also detected with a UV-Vis light spectrometer (Hitachi, U-3900), which were used to detect the absorbing property of the formed SOA.

95 The chemicals following were used without further purification: 1,3,5-trimethylbenzene (1,3,5-TMB) (99%, Acros), n-dodecane (>99%, Alfa Aesar), sulfuric acid (>95%, Beijing Chemical Works), sodium nitrite (98%, Alfa Aesar), methanol (99.9%, Merck), acetonitrile (99.8%, Fisher Chemical).



## 2.2 Calculation Methods

### 2.2.1 Wall-Loss Corrections

100 As SOA yields could be underestimated due to the losses of SOA forming vapors to chamber walls, the vapor wall-loss was considered and corrected in this work (Zhang et al., 2014). The competition between the uptake of organic vapor by the chamber walls and the aerosol particles would determine the effect of vapor wall-loss on SOA yields (Zhang et al., 2015b). The ratio of average gas-particle partitioning timescale ( $\bar{\tau}_{g-p}$ ) to the vapor wall-loss timescale ( $\bar{\tau}_{g-w}$ ) could be used to evaluate the underestimation of SOA yields (Zhou et al., 2011; Chen et al., 2019).

105 The average gas-particle partitioning timescale ( $\bar{\tau}_{g-p}$ ) could be expressed as the following equation (Seinfeld J.H., 2006; Zhang et al., 2014):

$$\bar{\tau}_{g-p} = \frac{1}{2\pi\bar{N}_p\bar{D}_pD_{gas}\bar{F}_{FS}} \quad (1)$$

where  $\bar{N}_p$  was the average number concentration of the formed particles during the experiment,  $\bar{D}_p$  was the number mean diameter of the particles,  $D_{gas}$  was the gas-phase diffusivity,  $\bar{F}_{FS}$  was the Fuchs-Sutugin correction for noncontinuum mass transfer (Seinfeld J.H., 2006).

The vapor wall-loss timescale ( $\bar{\tau}_{g-w}$ ) could be expressed as the following equation (Zhang et al., 2015b):

$$\bar{\tau}_{g-w} = \frac{1}{k_w} \quad (2)$$

$$k_w = \left(\frac{A}{V}\right) \frac{a_w\bar{c}}{1.0 + \frac{\pi}{2} \left[ \frac{a_w\bar{c}}{4(k_e D_{gas})^{0.5}} \right]} \quad (3)$$

115 where  $k_w$  was the wall loss rates of the organic vapor;  $\frac{A}{V}$  was the ratio of surface to volume of the chamber,  $1.55 \text{ m}^{-1}$  for this chamber;  $a_w$  was the mass accommodation coefficient of vapors deposition to the wall ( $10^{-5}$  was used here) (Zhang et al., 2014);  $\bar{c}$  was the root mean square speed of the gas;  $k_e$  was the eddy diffusion coefficient, which was set to  $0.12 \text{ s}^{-1}$  according to the reported values for a  $60 \text{ m}^3$  chamber (McMurry and Grosjean, 1985). The detailed calculation of  $\bar{c}$ ,  $D_{gas}$ ,  $k_n$  and  $\bar{F}_{FS}$  were shown in the Supporting Information.

120 Particle wall-loss to chamber walls would also cause underestimation when calculating the SOA yield from measurements if these losses were not corrected for. Thus particle wall-loss was accounted for during the experiments. The particle wall-loss was treated as a first-order process, and the wall-loss coefficient ( $k_{dep}$ ) could be expressed as the following equation:

$$\ln \frac{A_0}{A_T} = k_{dep}t \quad (4)$$

125 where  $A_0$  was the mass concentration at time  $t_0$ , and  $A_T$  was the mass concentration at time  $t$ . According to the wall-loss of ammonium sulfate particles (Li et al., 2021), the wall-loss rate  $k_{dep}$  was set to  $0.23 \text{ h}^{-1}$  for the experiments in this chamber.



### 2.2.2 SOA Yields

The secondary organic aerosol (SOA) yield ( $Y$ ) was defined as the fraction of a reactive organic gas (ROG) that was converted to aerosol, and it could be calculated by the following equation:

$$Y = \frac{\Delta M_o}{\Delta ROG} \quad (5)$$

130 where  $\Delta M_o$  ( $\mu\text{g m}^{-3}$ ) was the mass concentration of the organic aerosol, and  $\Delta ROG$  ( $\mu\text{g m}^{-3}$ ) was the amount of the ROG reacted.

For the mixed anthropogenic volatile organic compounds (AVOCs), the formed SOA mass was predicted based on the SOA precursors and their SOA yield measured in this study. The possible non-linear interactions between the anthropogenic VOC mixtures were not taken into account. Specifically, the calculation equation (Kari et al., 2019) could be expressed as  
135 follows:

$$SOA_{predicted} = \sum_i(\Delta ROG_i \times Y_i) \quad (6)$$

where  $\Delta ROG_i$  was the amount of the  $ROG_i$  reacted, and  $Y_i$  was the SOA yield of  $ROG_i$ .

## 3 Results and Discussion

A set of experiments are conducted in summer, of which the initial conditions and general results are shown in Table 1. The  
140 experiments are conducted as follows: n-dodecane + HONO; 1,3,5-trimethylbenzene + HONO; n-dodecane + 1,3,5-trimethylbenzene + HONO. The experiments are conducted under similar conditions, and the details of the relative humidity (RH), temperature (T), and the  $\text{NO}_2$  photolysis rate ( $J(\text{NO}_2)$ ) of the experiments are shown in Figure S1. The  $\text{NO}_2$  photolysis rates of the experiments at noon in summer are in the range of  $0.005\text{--}0.006 \text{ s}^{-1}$ ; for the experiment MIX-3, the weather is cloudy, and the  $J(\text{NO}_2)$  at noon is relatively smaller,  $0.004 \text{ s}^{-1}$ . The temperature in summer at noon is in the range of  $30\text{--}46 \text{ }^\circ\text{C}$ ,  
145 the RH inside the chamber is  $< 10\%$ . The reactions profiles of photo-oxidation of n-dodecane, 1,3,5-TMB, and mix AVOCs under HONO conditions in summer are shown in Figure 1.

The SOA yields of n-dodecane and 1,3,5-TMB are  $16.4\text{--}21.9\%$  and  $4.1\text{--}5.6\%$ , respectively, as shown in Table 1. The predicted SOA mass derived from the mixture of these VOCs is based on the measured SOA yields of n-dodecane and 1,3,5-TMB, without considering possible non-linear interactions between them. Then the observed SOA mass is compared to  
150 the predicted values. It can be seen that nearly all the measured values are higher than the predicted SOA mass both before and after wall-loss correction. In other words, the SOA formation is enhanced when the two AVOCs are mixed together, indicating the potential synergistic effect may exist in the mixed AVOCs reaction system. The findings above would be discussed further in the following parts.



### 3.1 Enhancement of SOA formation

155 Figure 1 shows the formation and evolution of the SOA during the photochemical reaction processes in summer. The  
number mean diameter, number concentration, surface mean diameter, total surface, and mass concentration of the particles  
are analyzed and compared. The number mean diameters of the formed particles from n-dodecane, 1,3,5-TMB, and the  
mixture are 100 nm, 50-100 nm, and 150-200 nm, respectively. This suggests that after mixing the two precursors, the  
number mean diameter of the formed particle became larger. The number concentration of the formed particles, similarly,  
160 increased from  $2.0 \times 10^3 \text{ \#/cm}^3$  for single precursors to above  $1.0 \times 10^4 \text{ \#/cm}^3$  for mixture. Because of the enhanced particle  
number concentration and diameter, the mass concentration of particle increases from  $< 4 \text{ \mu g/m}^3$  for individual precursors to  
 $> 40 \text{ \mu g/m}^3$  for mixture. It can be seen that the mass concentration of SOA generated by the mixed AVOCs system is  
significantly higher than the sum of the SOA generated by the two separate systems. It should be noted that the surface mean  
diameter of the particles from n-dodecane, 1,3,5-TMB, and the mixed AVOCs is all around 200 nm. However, due to the  
165 enhanced number concentration for mixture, the total surface of the formed particles for mixture ( $> 1.0 \times 10^9 \text{ nm}^2/\text{cm}^3$ ) was  
higher than individual precursors ( $< 1.0 \times 10^8 \text{ nm}^2/\text{cm}^3$  for n-dodecane;  $< 5.0 \times 10^7 \text{ nm}^2/\text{cm}^3$  for 1,3,5-TMB). Overall, after  
the two precursors are mixed, the number mean diameter, number concentration, total surface, and mass concentration of the  
generated particles were improved, while the surface mean diameter of the particles did not change.

From the results shown above, we know that the SOA yield is significantly enhanced when mix n-dodecane and 1,3,5-  
170 TMB together. Experimental conditions can influence the SOA yields; however, they only change little on the SOA yield.  
First, precursor concentration may play a role; however, we can rule it out based on the analysis below. Several previous  
studies (Lauraguais et al., 2012; Loza et al., 2014; Zhou et al., 2011; Ng et al., 2007a) have reported that the aerosol  
formation is strongly affected by the initial precursor concentration, with higher initial concentration of precursor leading to  
higher SOA yields. As higher initial precursor concentration will produce a higher amount of condensable products through  
175 chemical processes, thus the formed SOA mass will be higher. The aerosol present in the system will directly affect the gas-  
particle partitioning, as the medium, it can adsorb the oxidation products; thus, higher SOA mass will lead to higher SOA  
yield (Lauraguais et al., 2014). In this work, for TMB-1 and TMB-2, while keeping the HONO concentration basically  
unchanged, the concentration of 1,3,5-TMB increases from 105 ppb ( $514.5 \text{ \mu g/m}^3$ ) to 178 ppb ( $882.9 \text{ \mu g/m}^3$ ), the yield  
increases by only 1.5%. For the mixed AVOCs reaction system, the concentrations of the precursors for MIX-1 and MIX-2  
180 are 168 and 155 ppb ( $824.2$  and  $756.2 \text{ \mu g/m}^3$ , 1,3,5-TMB), 28 and 22 ppb ( $194.7$  and  $152.3 \text{ \mu g/m}^3$ , n-dodecane), respectively.  
Compared with TMB-2 experiments, the concentration of MIX precursor is only increased about  $136 \text{ \mu g/m}^3$  and  $25.6 \text{ \mu g/m}^3$   
(3%-15%). According to the SOA yields of TMB reaction system, the increase in the precursors mass concentration of the  
mixed system is not the reason for the large increase in the SOA mass concentration. Second, NO<sub>x</sub> may also influence the  
SOA yield, but likely not this case here. Tsiligiannis et al. (2019) observed that the particle formation strongly varied with  
185 NO<sub>x</sub> conditions, the increasing NO<sub>x</sub>/ΔTMB ratio would suppress the SOA formation. In this work, regardless of whether it  
is a single or a mixed reaction system, the NO<sub>x</sub> concentration in the system remains basically unchanged. For experiments



TMB-2, MIX-1, and MIX-2, they have the similar  $\Delta\text{VOC}/\text{NO}_x$  ratio, all around  $\sim 8$ , but the formed SOA mass concentration is quite different. This indicates that the  $\Delta\text{VOC}/\text{NO}_x$  ratio here has little effect on the enhanced SOA mass concentration of the mixed AVOCs reaction system.

190 For the enhancement in SOA yield of the mixed AVOCs system, we propose two possible conjectures, as revealed in Figure 2. The first conjecture is that the gas-particle partitioning of the system has changed. The SOA yield of n-dodecane (16-22%) is significantly higher than that of 1,3,5-TMB (4-6%), so the volatility of its products (including gas phase and particle phase) is relatively lower, and it is easier to form particles, e.g., nucleation; for the 1,3,5-TMB reaction system, the products has higher volatility and are difficult to condense and nucleate, so the yield is lower. When 1,3,5-TMB is mixed  
195 with n-dodecane, the products of n-dodecane provide a lot of particles for the products of 1,3,5-TMB to coagulate, so the yield is greatly improved. Another conjecture is that there are chemical interactions between the two systems, i.e., the intermediate products of the two precursors may react with each other.

In order to know which conjecture is correct, the injection experiments are performed: n-dodecane and HONO are introduced into the chamber firstly, and after one (Figure 3c and d, MIX-6) or four (Figure 3a and b, MIX-7) hours of photochemical reaction, 1,3,5-TMB is introduced into the chamber. As shown in Figure 3a and c, after the introduction of  
200 1,3,5-TMB, the mass and number concentration of the particles has a certain increase, and the consumption of  $\text{NO}_x$  is accelerated. However, compared with Figure 3e (n-dodecane and 1,3,5-TMB are added together before the photochemical experiments, MIX-4), the final SOA mass concentration of MIX-6 and MIX-7 (Figure 3a and c) are much lower. If our first conjecture plays an important role, one would expect large SOA mass enhancement (similar with mixed experiments) as the  
205 products of n-dodecane provide enough condensational sink for 1,3,5-TMB products to condense. The result here indicates that the gas-particle partitioning conjecture plays a minor role in the SOA yield enhancement. In order to further verify our second conjecture, the particle compositions are analyzed and shown below.

Figure 4 shows the ESI-TOF-MS mass spectra of SOA generated from n-dodecane, 1,3,5-TMB, and mixed AVOCs. The representative identified products with strong intensity are shown in Figure S2 and Table 2. The identified products are  
210 mainly based on the mass spectra and previous related studies (Tsiligiannis et al., 2019; Li et al., 2017a; Sato et al., 2019).

Huang et al. (2015) reported that the predominant products for aging of 1,3,5-trimethylbenzene secondary organic aerosol were organic nitrogen-containing products, aromatic organic acid, oxocarboxylic acid, and oligomer compounds. Due to the various  $\text{NO}_x/\Delta\text{TMB}$  ratios, the formed products might be different. Usually, higher  $\text{NO}$  would lead to the suppression of oligomers and particle formation, and higher  $\text{NO}$  would result in an increase in the formation of organonitrates (Tsiligiannis et al., 2019). The products derived from n-dodecane in the presence of  $\text{NO}_x$  were mainly oxygen-containing organic compounds (i.e., peroxyhemiacetals, hemiacetals, esters, aldol condensation) and organonitrate  
215 products (Fahnestock et al., 2015; Lim and Ziemann, 2005).

As shown in Figure 4, most products from n-dodecane, 1,3,5-TMB, and mixed AVOCs SOA are concentrated around  $m/z$  200-450. In the range of  $m/z$  500-700, oligomers are formed. As shown in Table 2, the products derived from 1,3,5-  
220 TMB are mainly organonitrates and oxygen-containing organic compounds. For products derived from n-dodecane, the main



components are also oxygen-containing organic compounds and organic nitrates. It should be noted that in the reaction system of mixed AVOCs, there are some products that are not detected in the separate reaction system (n-dodecane or 1,3,5-TMB), such as  $C_{16}H_{30}O_4$ ,  $C_{29}H_{48}O_{10}$ ,  $C_{35}H_{68}O_{10}$ , etc. This indicates that interactions occur between the intermediate products from n-dodecane and 1,3,5-TMB. Some substances with higher volatility (which may exist in the gas phase in a separate reaction system) could participate in the reaction and enter the particle phase, thereby increasing the SOA mass concentration. And this could be the main reason that the measured SOA mass concentration derived from mixed AVOCs reaction system higher than the predicted mass concentration.

### 3.2 Light absorption of secondary organic aerosol

Figure 5 shows the UV-Vis spectra of the n-dodecane, 1,3,5-TMB, and mixed AVOCs SOA filter extract. Before analyzing the samples, the blank PTFE membrane filter is dissolved with methanol, and the ultraviolet-visible absorption spectrum of the methanol solution is analyzed. It could be seen from the UV-Vis spectra that all SOA filter solutions has no light absorption in the wavelength of 300-600 nm. The absorption is mainly concentrated in the wavelength of  $< 300$  nm. This is consistent with previous literature reports: Li et al. (2017a) found that the n-dodecane SOA solutions had no detectable absorption in the wavelength of  $> 350$  nm; Huang et al. (2018) found that the 1,3,5-TMB SOA solutions also had no obvious absorption in the wavelength of  $> 300$  nm.

As shown in Figure 5, all the SOA solutions has obvious optical absorption around 205 nm. According to literature reports, the absorption at 205 nm corresponds to the carboxyl compound (Carlton et al., 2007; Huang et al., 2018). This indicates that the SOA particles derived from n-dodecane, 1,3,5-TMB, and mixed AVOCs may contain carboxyl compounds. This is consistent with literature reports: Huang et al. (2015) found that the predominant products of the aging 1,3,5-TMB particles under high  $NO_x$  conditions were 3,5-dimethylbenzoic acid, 2,4-dimethyl-2,3,4-trihydroxy-5,6-dioxo-heptylic acid, etc.; Fahnstock et al. (2015) reported that under high NO conditions, the carboxyl compounds could be formed from n-dodecane, e.g., the carboxylic acids, esters, carboxylic acid anhydrides. Compared to the n-dodecane and 1,3,5-TMB reaction systems, the mixed AVOCs reaction system formes more carboxyl compounds, as revealed by Figure 5.

Meanwhile, the SOA particle solutions has absorption around 230 nm, as shown in Figure 5. According to the absorption characteristics of the ultraviolet-visible spectrum, if there is a strong absorption at 210-250 nm, indicating that there is a K absorption band, it may contain a conjugated system of two double bonds, such as conjugated diene or  $\alpha,\beta$ -unsaturated ketone. This indicates that the compounds containing a conjugated system of two double bonds are existed in the aging SOA particles, and the relative strength is mixed AVOCs SOA  $>$  n-dodecane SOA  $>$  1,3,5-TMB SOA. Such substances had also been reported in previous literatures (Li et al., 2017a; Fahnstock et al., 2015; Huang et al., 2015)

### 3.3 Factors affecting the formation of SOA and ozone

According to previous studies, ozone concentration was statistically positively correlated with temperature, solar radiation intensity, and sunshine hours, and was negatively correlated with precipitation, relative humidity (RH), visibility, and wind



speed (Wang et al., 2017; Huang et al., 2019; Jaffe and Zhang, 2017). In this work, the factors affecting ozone generation considered in this work mainly included solar radiation intensity, temperature, and precursor concentrations. Figure 6 showed the generation of ozone during the photochemical reactions of three different reaction systems. As shown in Figure 6 (a), for n-dodecane reaction system, the ozone concentration was Dod-1 > Dod-2. As revealed by Table S2 and Figure S1, under similar  $\Delta\text{VOCs}/\text{NO}_x$  ratio and solar radiation intensity ( $J(\text{NO}_2)$ ), higher temperature would promote the formation of ozone. For 1,3,5-TMB reaction system, the formed ozone concentration followed the order: TMB-2 > S-TMB-3 > TMB-1. The corresponding  $\Delta\text{VOCs}/\text{NO}_x$  ratio were 8.13, 6.12, and 4.48, respectively. The temperature conditions were TMB-1 > TMB-2 > TMB-3. The  $J(\text{NO}_2)$  was similar for the three experiments. With the similar solar radiation intensity, the  $\Delta\text{VOCs}/\text{NO}_x$  ratio of precursors played a decisive role in the generation of ozone concentration compared to the temperature conditions. For mixed AVOCs reaction system, the order of formed ozone concentration was MIX-2 > MIX-1. The corresponding  $\Delta\text{VOCs}/\text{NO}_x$  ratio was 7.83 and 8; the  $J(\text{NO}_2)$  was MIX-1 ~ MIX-2. The TMB/Dod ratio were 7 and 6. This indicated that, under similar  $\Delta\text{VOCs}/\text{NO}_x$  ratio and  $J(\text{NO}_2)$  conditions, higher TMB/Dod ratio would promote the formation of ozone. For experiments MIX-2 and MIX-3, the  $\Delta\text{VOCs}/\text{NO}_x$  ratio were similar, the temperature conditions were MIX-2 > MIX-3, the  $J(\text{NO}_2)$  was MIX-2 ~ MIX-3, the TMB/Dod ratio were 9.1 and 7. The conditions above indicated that the higher TMB/Dod ratio played a decisive role in the generation of ozone concentration. In conclusion, lower temperature and higher  $\Delta\text{VOCs}/\text{NO}_x$  (ppbC/ppb) ratio in a separate reaction system will promote the particle formation; the relative content of reaction precursors (ppb/ppb) in the mixed system will affect the formed particles, with similar  $\Delta\text{VOCs}/\text{NO}_x$  ratio, higher concentration of n-dodecane would promote the generation of particles; reaction conditions have little effect on the size of the final particle size.

As shown in Figure 7, for n-dodecane reaction system, the mass concentration, number concentration, and total surface of the particles were Dod-1 < Dod-2. According to Figure S1 and Table S2, under similar  $\Delta\text{VOCs}/\text{NO}_x$  ratio and  $J(\text{NO}_2)$ , lower temperature would promote the formation of particles. However, the surface mean and number mean diameter of the two experiments were around 100 and 200 nm, this indicated that temperature had little effect on the diameter of the formed particles. For 1,3,5-TMB reaction system, under similar  $J(\text{NO}_2)$ , lower temperature and higher  $\Delta\text{VOCs}/\text{NO}_x$  ratio would promote the particle formation; temperature and  $\Delta\text{VOCs}/\text{NO}_x$  ratio had little effect on the particle diameters. For the mixture experiments, under similar  $\Delta\text{VOCs}/\text{NO}_x$  ratio, compared with  $J(\text{NO}_2)$  and temperature, higher Dod/TMB ratio would promote the particle formation; similarly, the above conditions had little effect on the particle size. In conclusion, higher temperature and higher  $\Delta\text{VOCs}/\text{NO}_x$  (ppbC/ppb) ratio in a separate reaction system will promote the generation of ozone; the relative content of reaction precursors (ppb/ppb) in the mixed system will affect the concentration of ozone, with similar  $\Delta\text{VOCs}/\text{NO}_x$  ratio, higher concentration of 1,3,5-TMB will promote ozone generation.

#### 4 Atmospheric Implications



285 Our findings demonstrate that the SOA yield derived from the mixed anthropogenic volatile organic compounds (n-dodecane  
+ 1,3,5-TMB) in the presence of HONO is higher than the predicted value. The results of this work further demonstrate the  
inaccuracy of the SOA yield calculation method for the VOCs mixture, i.e., the simple linear addition of SOA yields from  
the individual yield of the compound in the VOCs mixture. This calculation method may underestimate or overestimate the  
SOA production. In this work, the SOA production from the mixed n-dodecane and 1,3,5-TMB is underestimated. In the  
290 general case, the SOA yields from the individual compounds should be used with caution when calculating the SOA yields  
from VOCs mixture. In addition, as the representative substances of motor-vehicle exhaust, long-chain alkanes and aromatic  
hydrocarbons exist in the atmospheric at the same time. The increase in SOA yield after mixing the two kinds of compounds  
gives us an insight on the SOA yield derived from motor-vehicle exhaust. Our results indicate that SOA formation needs to  
be considered more realistically in the atmosphere.

## 295 **5 Conclusions**

In summary, a set of photochemical experiments are carried out in a large scale outdoor smog chamber. The measured SOA  
mass concentration of the mixed AVOCs (n-dodecane + 1,3,5-TMB) is compared to the predicted SOA mass concentration  
based on the SOA mass yields of the individual compounds. Results show that the SOA formation from the mixed AVOCs is  
enhanced. Mass spectra of the SOA particles indicates that interaction occur between the intermediate products from the two  
300 precursors, and the products previously present in the gas-phase may enter the particle-phase through this inter-reaction. This  
could be the main reason for the enhanced SOA production from the mixed AVOCs reaction system. UV-Vis spectra of the  
n-dodecane, 1,3,5-TMB, and mixed AVOCs SOA filter extract indicates that absorptive products were mainly compounds  
with carboxyl functional groups and conjugated double bond functional groups. The SOA formation and the ozone formation  
varies with the NOX/VOCs ratio, the temperature, and the solar radiation intensity.

305 Further research is needed to study the SOA chemistry from biogenic-biogenic VOC mixtures, biogenic-anthropogenic  
VOC mixtures, and anthropogenic-anthropogenic VOC mixtures. The interactions between them and the effect on SOA  
formation are needed to be determined.

*Data availability.* The data used in this study are available upon request from the corresponding author.

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*Author contributions.* Junling Li and Hong Li conceived and led the studies. Junling Li, Kun Li, Yan Chen, Hao Zhang, Xin  
Zhang and Zhenhai Wu performed chamber simulation and data analysis. Hong Li, Yongchun Liu, Xuezhong Wang,  
Weigang Wang, and Maofa Ge discussed the results and commented on the paper. Junling Li prepared the article with  
contributions from all coauthors.

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*Competing interests.* The authors declare that they have no conflict of interest.



*Acknowledgements.* This project was supported by the Beijing Municipal Science & Technology Commission (No. Z181100005418015) and China Postdoctoral Science Foundation (2019M660752). We would like to thank Mr. Liang Bin  
320 from Bruker for supporting us in mass spectrometry analysis.

*Financial support.* This project was supported by the Beijing Municipal Science & Technology Commission (No. Z181100005418015) and China Postdoctoral Science Foundation (2019M660752).

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**Table 1. Summary of the initial conditions and results of the conducted experiments.**

Number	Date	Initial Conditions of the Experiments									General Results of the Experiments					
		1,3,5-TMB (ppb)	<i>n</i> -dodecane (ppb)	NO (ppb)	NO <sub>2</sub> (ppb)	NO <sub>x</sub> (ppb)	Δ VOCs/NO <sub>x</sub> (ppbC/ppb)	T (at noon) (°C)	J(NO <sub>2</sub> ) (at noon) (s <sup>-1</sup> )	RH (%)	O <sub>3</sub> (ppb)	Mass <sup>a</sup> (μg/m <sup>3</sup> )	Mass Predicted <sup>b</sup> (μg/m <sup>3</sup> )	Mass Corr. <sup>c</sup> (μg/m <sup>3</sup> )	Mass Predicted <sup>d</sup> (μg/m <sup>3</sup> )	Yield <sup>e</sup> (%)
Dod-1	2019.09.27	--	22	50	160	210	1.26	37	0.0050	< 2	57	6.4	--	33.5	--	21.9
Dod-2	2019.10.09	--	20	77	137	214	1.12	34	0.0048	< 2	25	3.7	--	22.3	--	16.4
TMB-1 (Li et al., 2021)	2019.09.03	105	--	23	188	211	4.48	43	0.0056	< 4	288	2.1	--	21.3	--	4.14
TMB-2 (Li et al., 2021)	2019.09.25	178	--	46	151	197	8.13	38	0.0053	< 4	772	5.1	--	49.8	--	5.6
TMB-3 (Li et al., 2021)	2019.10.14	170	--	68	182	250	6.12	30	0.0055	< 5	530	2.5	--	44.6	--	5.4
MIX-1	2019.09.07	168	28	62	169	231	8	46	0.0058	< 3	358	59.3	10.3	167.2	78.9	--
MIX-2	2019.09.21	155	22	58	154	212	7.83	39	0.0056	< 2	721	47.4	8.5	145.4	67.3	--
MIX-3	2019.09.19	182	20	71	147	218	8.61	31	0.0044	< 9	435	11.5	8.6	53.7	71.7	--
MIX-4	2020.08.21	251	35	54	158	212	12.64	39		< 7	999	60.2	13.7	150.1	108.7	--
MIX-5	2020.07.14	4 h add	27	61	157	218	--	52	0.0051	< 5	289	8	--	49.3	--	--
MIX-6	2020.07.20	4 h add	38	58	198	256	--	43	0.0057	< 4	276	6	--	35.2	--	--
MIX-7	2020.07.24	1 h add	39	56	207	263	--	42	0.0058	< 6	440	2.3	--	9.6	--	--
MIX-8	2020.07.22	227	1h add	48	167	216	--	43	0.0051	< 5	335	4.5	--	20.1	--	--

590 a: the mass here is the measured value with the SMPS; the density of the formed SOA derived from 1,3,5-TMB is assumed to be 1.4 g/cm<sup>3</sup> (Zhang et al., 2016; Nakao et al., 2013); the density of the formed SOA derived from *n*-dodecane is assumed to be 1.06 g/cm<sup>3</sup> (Lim and Ziemann, 2009; Li et al., 2017a); the density of the formed SOA derived from the mixed AVOCs is assumed to be 1.23 g/cm<sup>3</sup>.

b: the predicted mass here is based on the yield that the particle and vapor wall-loss are not considered.

c: the mass here is the value that the particle and vapor wall-loss are considered.

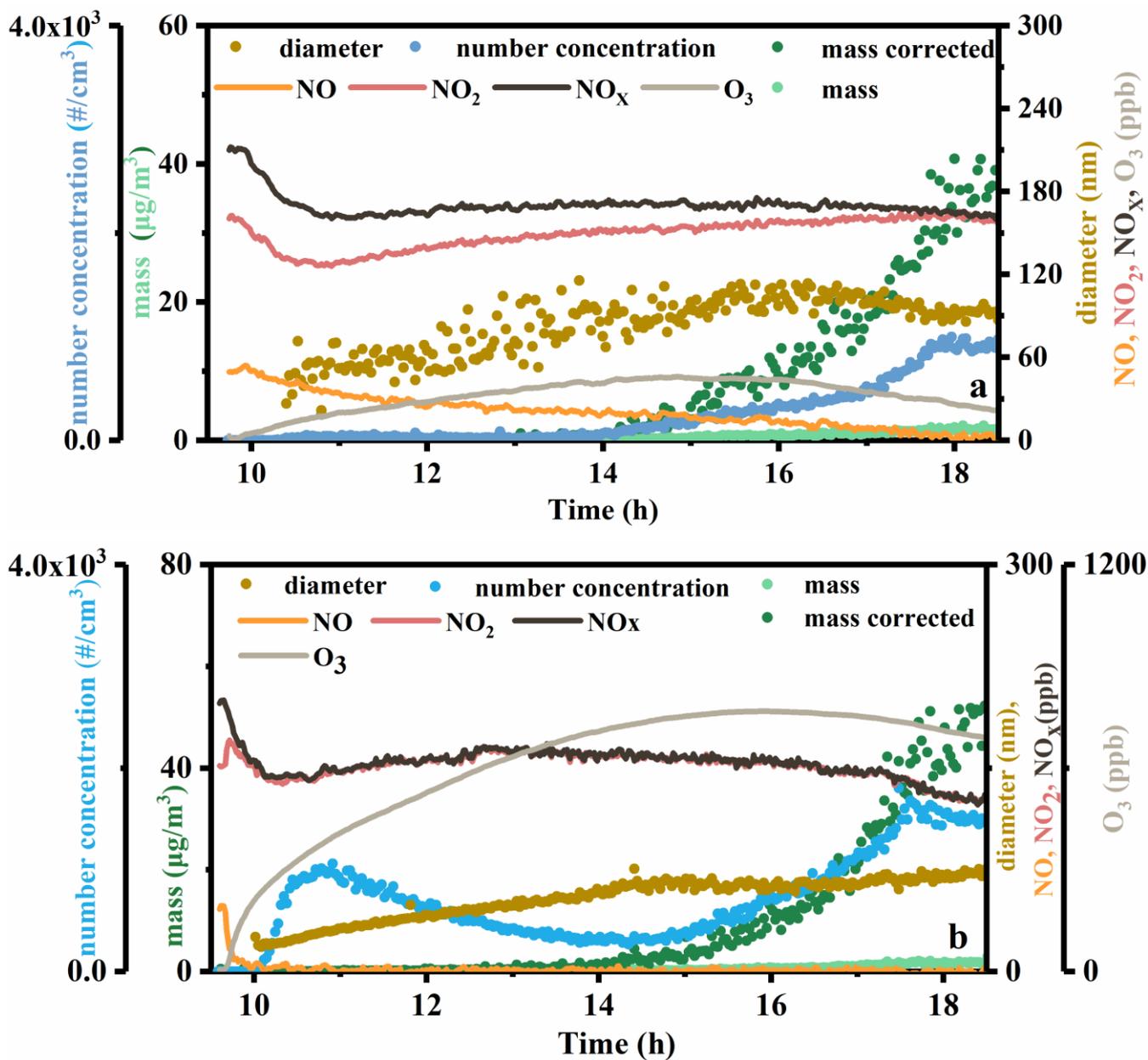
595 d: the predicted mass here is based on the yield that the particle and vapor wall-loss are considered.

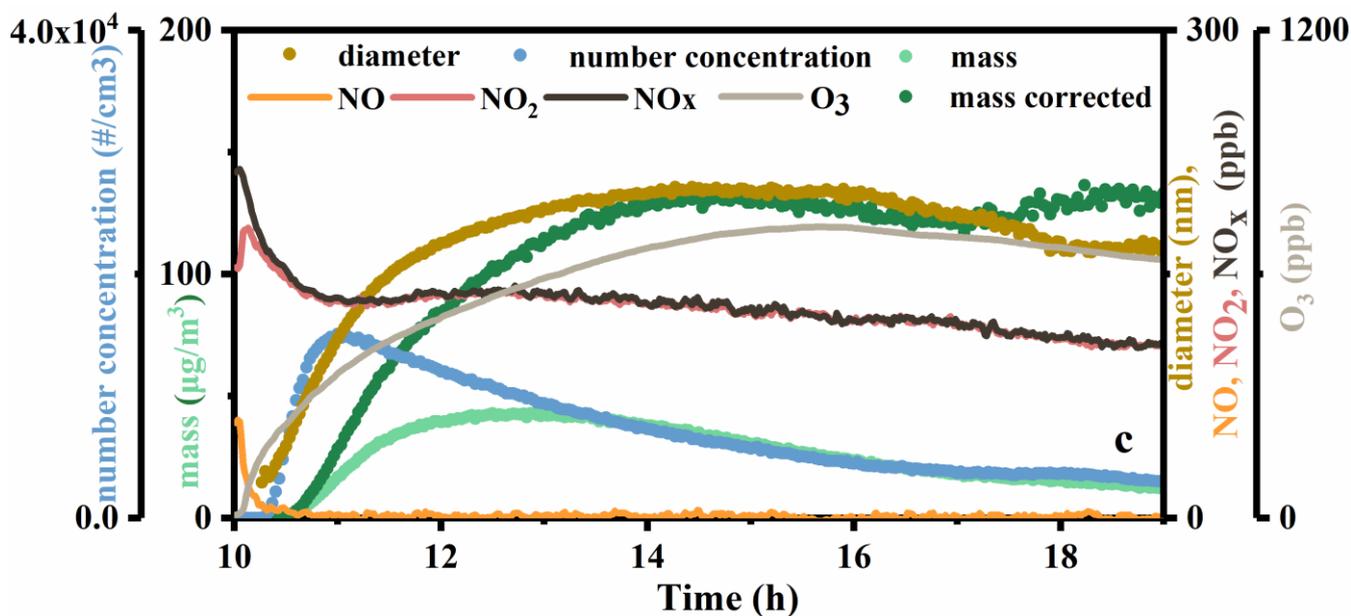
e: the yield here is based on the values that the particle and vapor wall-loss are considered.



600 **Table 2. Representative identified mass spectral peaks, molecular formulas, and molecular weights of *n*-dodecane, 1,3,5-TMB, and mixed AVOCs-derived SOA.**

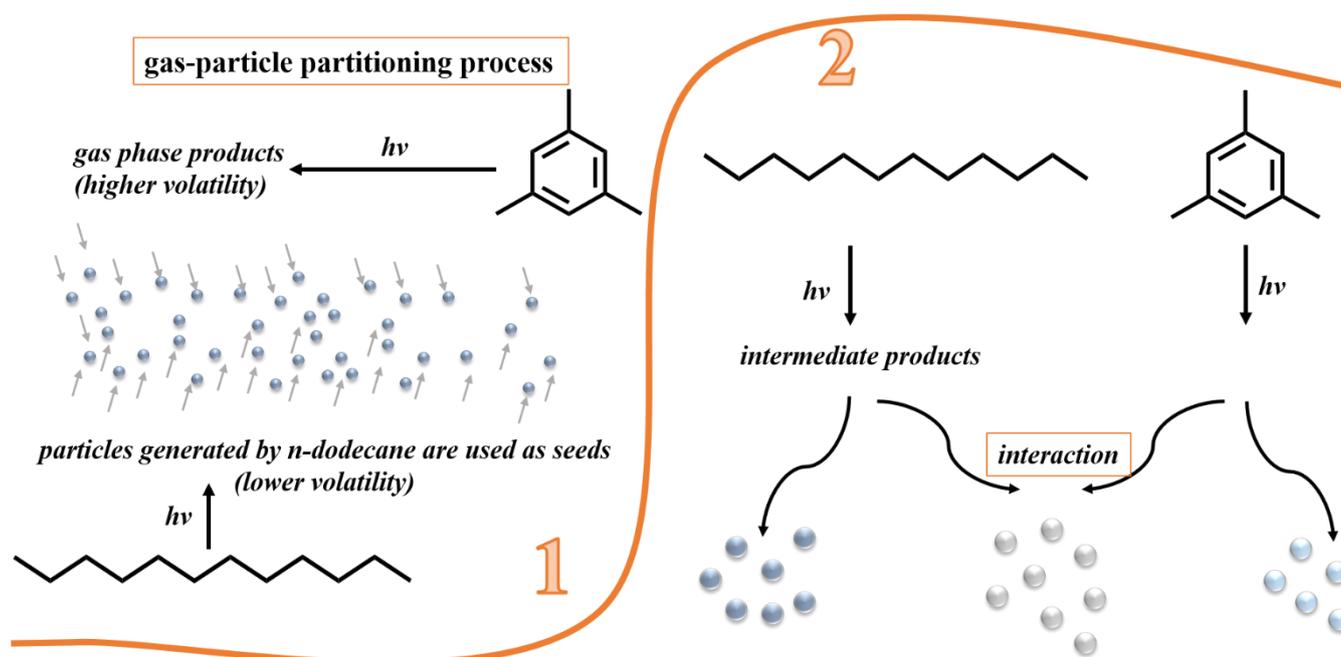
Molecular Formula	M+H	M+Na	MIX	TMB	<i>n</i> -dodecane
C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	171.099		√	√	
C <sub>9</sub> H <sub>17</sub> NO <sub>3</sub>		210.111		√	
C <sub>11</sub> H <sub>18</sub> O <sub>4</sub>	215.126		√		
C <sub>14</sub> H <sub>22</sub> O <sub>3</sub>	239.166		√		
C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>		243.134	√		√
C <sub>11</sub> H <sub>22</sub> NO <sub>5</sub>	249.158		√		
C <sub>14</sub> H <sub>26</sub> O <sub>2</sub>		249.183	√		
C <sub>13</sub> H <sub>25</sub> NO <sub>2</sub>		250.177	√	√	√
C <sub>8</sub> H <sub>12</sub> O <sub>9</sub>	253.056		√		
C <sub>11</sub> H <sub>22</sub> O <sub>5</sub>		257.135	√		
C <sub>12</sub> H <sub>20</sub> O <sub>6</sub>	261.131		√	√	√
C <sub>15</sub> H <sub>28</sub> O <sub>2</sub>		263.199	√		
C <sub>14</sub> H <sub>24</sub> O <sub>5</sub>	273.167		√		
C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	279.159		√	√	
C <sub>14</sub> H <sub>26</sub> O <sub>4</sub>		281.172	√		
C <sub>18</sub> H <sub>28</sub> O		283.207	√	√	√
C <sub>13</sub> H <sub>22</sub> NO <sub>6</sub>	289.153		√		
C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>		301.146	√	√	√
C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>		305.263	√	√	√
C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>		309.202	√		
C <sub>18</sub> H <sub>28</sub> O <sub>3</sub>		315.194		√	√
C <sub>16</sub> H <sub>24</sub> O <sub>5</sub>		319.151	√		
C <sub>20</sub> H <sub>34</sub> O <sub>2</sub>		329.246	√		√
C <sub>19</sub> H <sub>38</sub> O <sub>4</sub>		353.267	√	√	√
C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>		413.266	√	√	√
C <sub>20</sub> H <sub>34</sub> O <sub>8</sub>		425.214	√	√	
C <sub>24</sub> H <sub>36</sub> NaO <sub>5</sub>		427.245	√	√	
C <sub>27</sub> H <sub>48</sub> O <sub>8</sub>		523.325		√	√
C <sub>30</sub> H <sub>60</sub> NO <sub>6</sub>		553.459	√		√
C <sub>28</sub> H <sub>48</sub> O <sub>10</sub>		567.307	√		
C <sub>29</sub> H <sub>48</sub> O <sub>10</sub>		579.296	√		
C <sub>35</sub> H <sub>68</sub> O <sub>10</sub>		639.480	√		
C <sub>41</sub> H <sub>60</sub> NO <sub>6</sub>		685.434	√		√



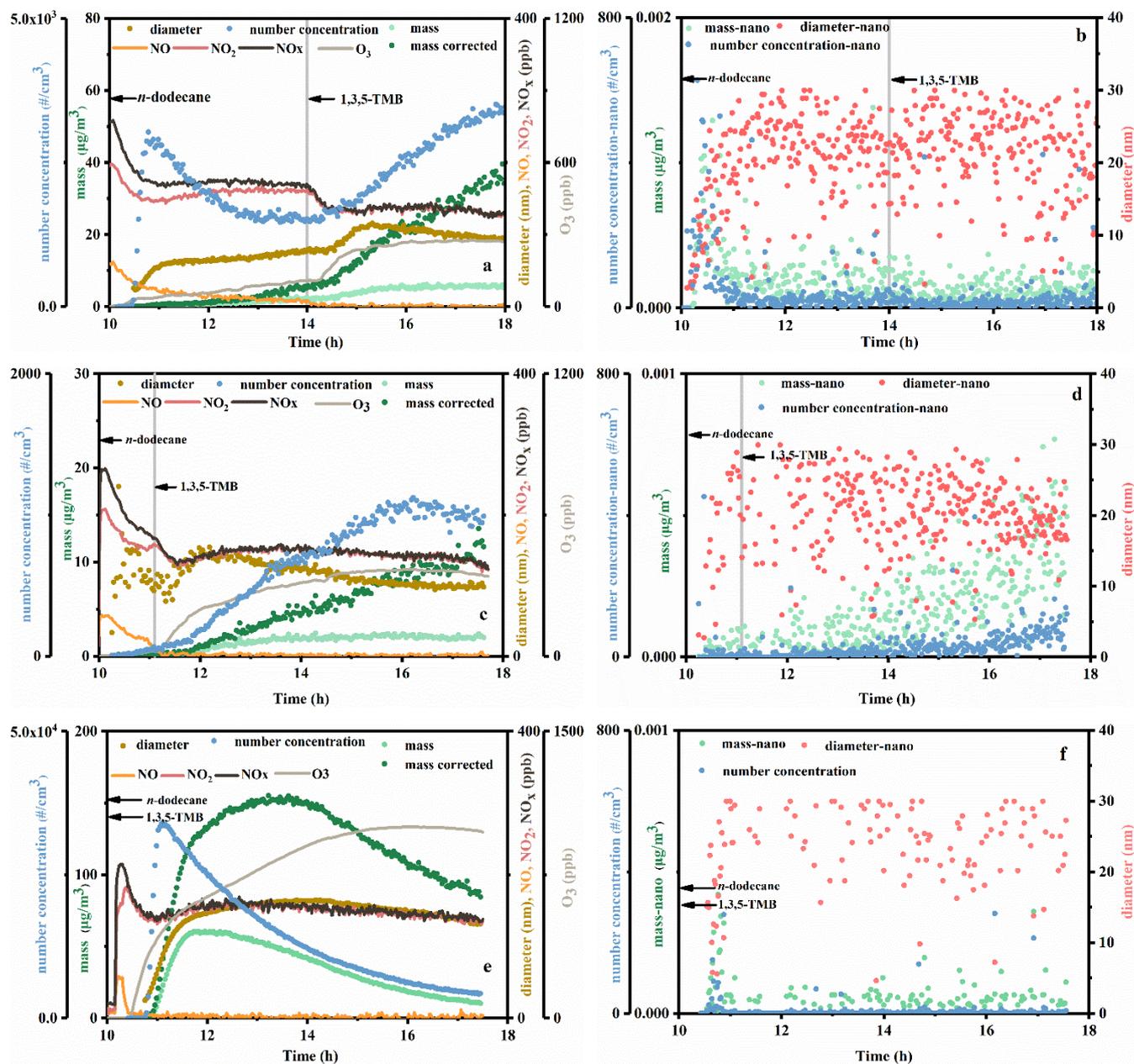


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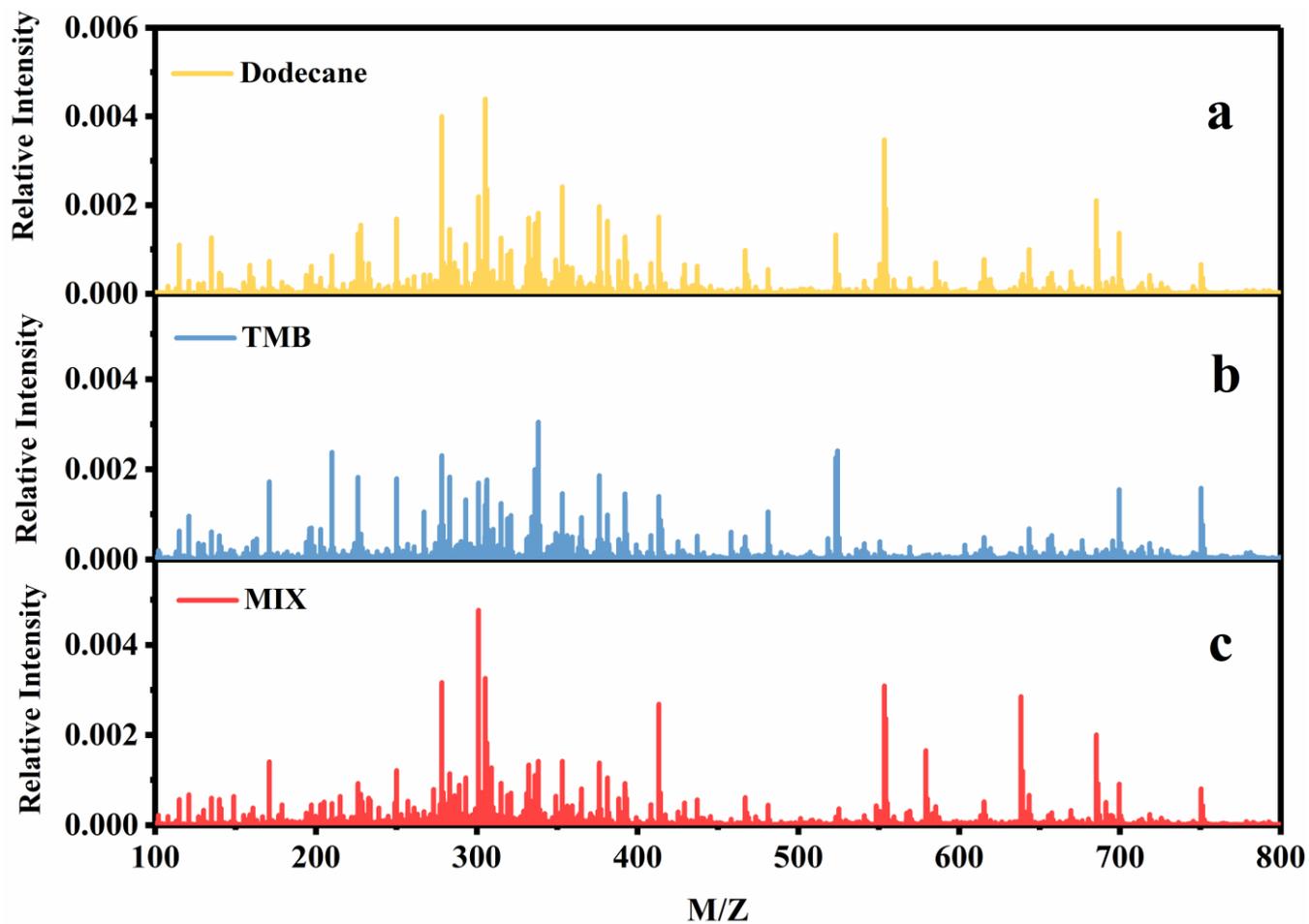
Figure 1. Reaction profiles of photooxidation of n-dodecane (a), 1,3,5-TMB (b), and mix AVOCs (c) under  $\text{NO}_x$  conditions in summer. The concentrations of mass and number concentration of particles are shown on the left axes, while the diameter of particles and concentrations of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_x$  and  $\text{O}_3$  are shown on the right axes.



615 Figure 2. The possible conjectures of the reaction processes.

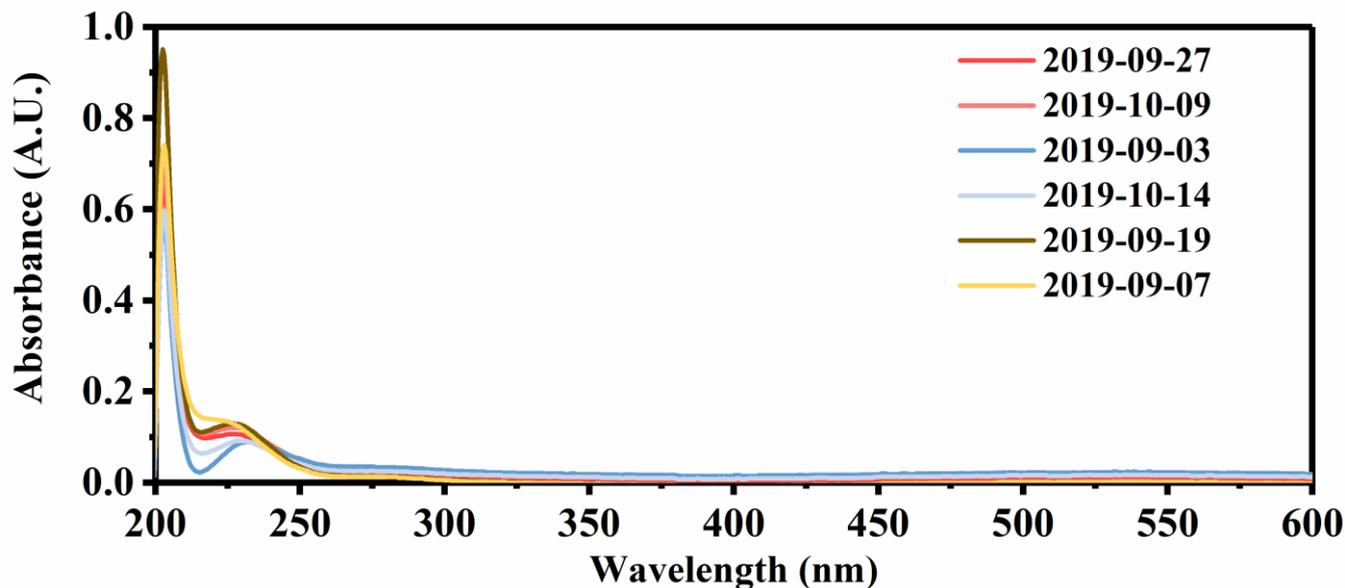


620 **Figure 3.** (a) reaction profiles of experiment MIX-6; (b) chagement of particles in the size range of 0-40 nm for MIX-6; (c) reaction profiles of experiment MIX-7; (d) chagement of particles in the size range of 0-40 nm for MIX-7; (e) reaction profiles of experiment MIX-4; (f) chagement of particles in the size range of 0-40 nm for MIX-4. The concentrations of mass and number concentration of particles are shown on the left axes, while the diameter of particles and concentrations of NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> are shown on the right axes. The vertical gray lines in the figures refer to the time that 1,3,5-TMB was added.



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Figure 4. Mass spectra of SOA generated from (a) *n*-dodecane, (b) 1,3,5-TMB, and (c) mixed AVOCs. The Y-axis is the relative intensity normalized by dividing by the total signal strength of the mass spectra.



630 Figure 5. UV-Vis spectra of the *n*-dodecane (2019-09-27, 2019-10-09), 1,3,5-TMB (2019-09-03, 2019-10-14), and mixed AVOCs (2019-09-19, 2019-09-07) SOA filter extract. The red lines refer to the *n*-dodecane SOA solutions, the blue lines refer to the 1,3,5-TMB SOA solutions, and the brown and yellow lines refer to the mixture AVOCs SOA solutions.

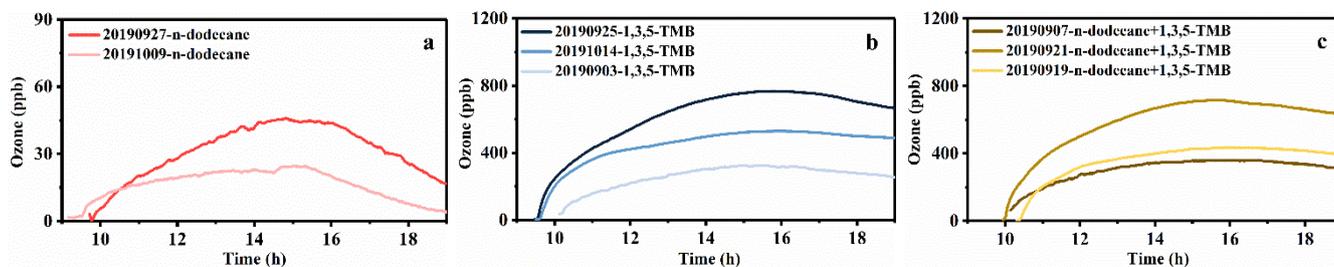
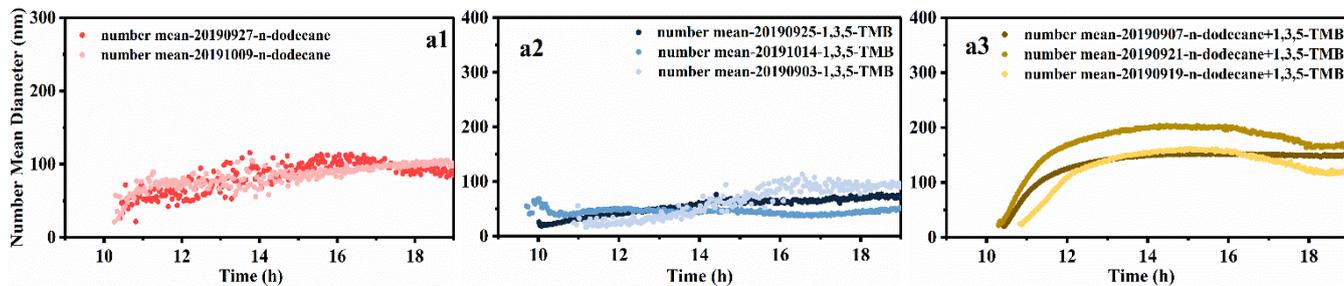
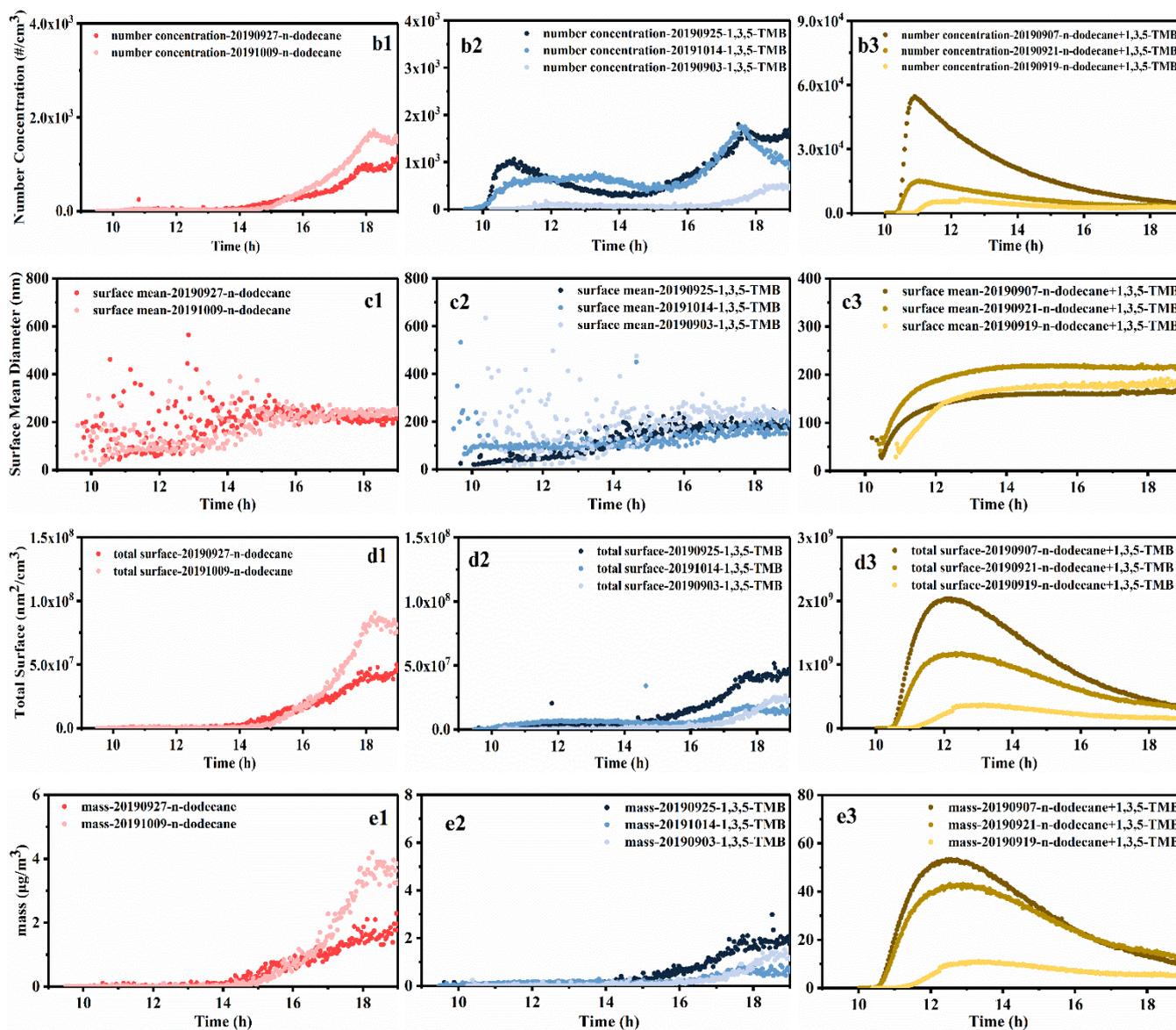


Figure 6. Ozone formation during the photochemical processes of the *n*-dodecane (a); 1,3,5-TMB (b); and mixed AVOCs (c).



635



640 **Figure 7.** The formation and evolution of particles during the photochemical reactions in summer. The number mean diameter of  
 particles derived from *n*-dodecane (a1), 1,3,5-TMB (a2), mixed AVOCs (a3); the number concentration of particles derived from  
*n*-dodecane (b1), 1,3,5-TMB (b2), mixed AVOCs (b3); the surface mean diameter of particles derived from *n*-dodecane (c1), 1,3,5-  
 TMB (c2), mixed AVOCs (c3); the total surface of particles derived from *n*-dodecane (d1), 1,3,5-TMB (d2), mixed AVOCs (d3);  
 the mass concentration of particles derived from *n*-dodecane (e1), 1,3,5-TMB (e2), mixed AVOCs (e3).

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